In re Patent Application of: Toshikazu Hamamoto et al.

Serial No. 09/569,185 Examiner: DOVE,TRACY MAE
Filed: May 11, 2000 Group Art Unit: 1745
For: NON-AQUEOUS ELECTROLYTE AND LITHIUM SECONDARY BATTERY USING THE SAME

TRANSLATOR'S DECLARATION

Honorable Commissioner of Patents & Trademarks
Washington, D.C. 20231

Sir:

I, Takashi Ishida , residing at c/o A. AOKI, ISHIDA & ASSOCIATES, Toranomon 37 Mori Bldg., 3-5-1, Toranomon Minato-ku, Tokyo 105-8423, Japan declare the following:

(1) That I know well both the Japanese and English languages;

(2) That I translated Japanese Patent Application No. 11-198351 , filed July 13, 1999 , from the Japanese language to the English language;

(3) That the attached English translation is a true and correct translation of the aforesaid Japanese Patent Application No. 11-198351 to the best of my knowledge and belief; and

(4) That all statements made of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements are made with the knowledge that willful false statements and the like are punishable by fine or imprisonment, or both, under 18 U.S.C. 1001, and that such false statements may jeopardize the validity of the application or any patent issuing thereon.

September 11, 2002
Date

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[Name of Article]	Specification	1
[Name of Article]	Abstract	1

[NEED FOR PROOF] Yes

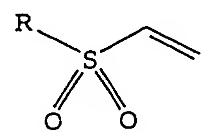
[NAME OF DOCUMENT] Specification

[TITLE OF INVENTION] Non-Aqueous Electrolyte And Lithium Secondary Battery Using The Same

[SCOPE OF CLAIM FOR PATENT]

[Claim 1] A non-aqueous electrolyte comprising an electrolyte salt dissolved in a non-aqueous solvent characterized in that the electrolyte salt is $LiBF_4$ and the non-aqueous solvent is mainly, composed of a cyclic carbonate and a cyclic ester and a vinyl sulfone derivative represented by the formula (I):

[Chemical 1]

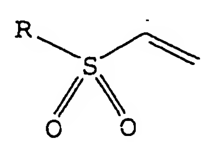


wherein R indicates a C_1 to C_{12} alkyl group, C_2 to C_{12} alkenyl group, or C_3 to C_6 cycloalkyl group, is contained in the electrolyte.

[Claim 2] A non-aqueous electrolyte as claimed in claim 1, wherein said non-aqueous solvent is mainly comprised of a cyclic carbonate, a cyclic ester and a linear carbonate.

[Claim 3] A lithium secondary battery provided with a cathode composed of a material containing a lithium composite oxide, an anode composed of a material containing carbon, a separator, and a non-aqueous electrolyte comprising an electrolyte salt dissolved in a non-aqueous solvent characterized in that the electrolyte salt is $LiBF_4$ and the non-aqueous solvent is mainly composed of a cyclic carbonate and a cyclic ester and a vinyl sulfone derivative represented by the formula (I):

[Chemical 2]



wherein R indicates a C_1 to C_{12} alkyl group, C_2 to C_{12} alkenyl

group, or C_3 to C_6 cycloalkyl group, is contained in the electrolyte.

[Claim 4] A lithium secondary battery as claimed in claim 3, wherein the non-aqueous solvent is mainly comprised of a cyclic carbonate, a cyclic ester and a liner carbonate.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field of the Invention]

The present invention relates to a non-aqueous electrolyte capable of providing a lithium secondary battery having superior battery cycle characteristic and battery characteristic such as electrical capacity, storage characteristic, and also relates to a lithium secondary battery using the same.

[0002]

[Prior Art]

In recent years, lithium secondary batteries have been widely used as the power sources for driving compact electronic devices etc. Lithium secondary batteries are mainly comprised of a cathode, a non-aqueous electrolyte and an anode. In particular, a lithium secondary battery having a lithium complex oxide such as $LiCoO_2$ as a cathode and a carbonaceous material or lithium metal as an anode is suitably used. Then, as the non-aqueous electrolyte for the lithium secondary battery, a composition comprising a combination of a cyclic carbonate such as ethylene carbonate (EC), propylene carbonate (PC) and a liner carbonate such as dimethyl carbonate (DMC), methylethyl carbonate (MEC), and diethyl carbonate (DEC) is suitably used.

On the other hand, as the salt dissolved in the non-aqueous solvent, a lithium salt such as $LiClO_4$, $LiPF_6$, $LiBF_4$ is used. A non-aqueous electrolyte containing such a non-aqueous solvent and the $LiPF_6$ dissolved therein is known to be high conductivity and high in the oxidation decomposition voltage of the $LiPF_6$, and therefore, is stable at high voltage.

[0003]

[Problems to be Solved by the Invention]

However, $LiPF_6$ is inferior in heat stability, and therefore, there is the problem that the lithium salt decomposed at a high temperature environment of 60°C or more and the battery performances such as the cycle life under a high temperature environment are tremendously decreased. On the other hand, $LiBF_4$, which is superior to $LiPF_6$ in the heat stability, may be mentioned, but since the ion conductivity that is inferior to that of $LiPF_6$, there is the problem that battery performance such as the cycle life is decreased under an ordinary temperature environment. Therefore, a cyclic ester such as γ-butyrolactone (GBL) is used due to the relatively high conductivity thereof. However, when GBL is used for a lithium secondary battery using a highly crystallized carbonaceous material such as natural graphite or artificial graphite as an anode, the GBL will electrochemically be decomposed at the graphite anode interface at the time of charging, and therefore, the battery performance will be decreased along with repeated use of charging and discharging. Thus, at the present time, the battery cycle characteristic and battery characteristics are not necessarily satisfactory.

[0004]

The object of the present invention are to solve the above-mentioned problems relating to an electrolyte for a lithium secondary battery and to provide a non-aqueous electrolyte for a lithium secondary battery having superior battery cycle characteristic and battery characteristics such as electrical capacity and a lithium secondary battery using the same.

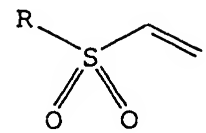
[0005]

[Means for Solving the Problems]

The present invention relates to provide a non-aqueous electrolyte comprising an electrolyte salt dissolved in a non-aqueous solvent characterized in that the electrolyte salt is $LiBF_4$ and the non-aqueous solvent is mainly composed of a cyclic carbonate and a cyclic ester and a vinyl sulfone

derivative represented by the formula (I):

[Chemical 3]

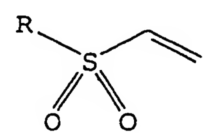


wherein R indicates a C_1 to C_{12} alkyl group, C_2 to C_{12} alkenyl group, or C_3 to C_6 cycloalkyl group, is contained in the electrolyte.

[0006]

The present invention also relates to a lithium secondary battery provided with a cathode composed of a material containing a lithium composite oxide, an anode composed of a material containing carbon, a separator, and a non-aqueous electrolyte comprising an electrolyte salt dissolved in a non-aqueous solvent characterized in that the electrolyte salt is $LiBF_4$ and the non-aqueous solvent is mainly composed of a cyclic carbonate and cyclic ester and a vinyl sulfone derivative represented by the formula (I):

[Chemical 4]



wherein R indicates a C_1 to C_{12} alkyl group, C_2 to C_{12} alkenyl group, or C_3 to C_6 cycloalkyl group is contained in the electrolyte.

In the preferred embodiments of the above non-aqueous electrolyte and the lithium secondary battery according to the present invention, the non-aqueous solvent is mainly composed of a cyclic carbonate, a cyclic ester, and optionally a linear carbonate and the electrolyte salt is $LiBF_4$.

[0007]

[Mode for Carrying Out the Invention]

The non-aqueous electrolyte of the present invention is used as a component member of a lithium secondary battery. The

component members of the secondary battery other than the non-aqueous electrolyte are not particularly limited. The various component members used in the past may be used.

[0008]

In the compound contained in the electrolyte composed of an electrolyte salt dissolved a non-aqueous solvent, the R in the vinyl sulfone derivative having the formula (I) is preferably a C_1 to C_{12} alkyl group such as a methyl group, ethyl group, or propyl group. The alkyl group may be a branched alkyl group such as an isopropyl group or isobutyl group. Further, it may be a C_2 to C_{12} alkenyl group such as a vinyl group or allyl group or a C_3 to C_6 cycloalkyl group such as a cyclopropyl group or cyclohexyl group.

[0009]

As specific examples of the vinyl sulfone derivative having the formula (I) are divinyl sulfone (R=vinyl group), ethylvinyl sulfone (R=ethyl group), isopropylvinyl sulfone (R=isopropyl group), cyclohexylvinyl sulfone (R=cyclohexyl group), etc. may be mentioned.

[0010]

In the case of adding the vinyl sulfone derivative, if the content of the vinyl sulfone derivative (I) is too large, the conductivity of the electrolyte etc. are varied and the battery performance is decreased in some cases. Further, if the content is too small, a sufficient coating is not formed and the expected battery performance cannot be obtained. Therefore, the content is preferably in the range of 0.01 to 20% by weight, particularly 0.1 to 10% by weight, based upon the weight of the electrolyte.

[0011]

The non-aqueous solvent preferably used in the present invention contains at least one of ethylene carbonate, propylene carbonate, and butylene carbonate, as a cyclic carbonate, and contains γ-butyrolactone and/or γ-valerolactone as a cyclic ester.

[0012]

By including the cyclic carbonate and cyclic ester and further a linear carbonate as the non-aqueous solvent in the present invention, it is possible to improve the wettability of the separator, reduce the variation at the time of production of the batteries, and raise the production efficiency and possible to improve the cycle characteristic. As the liner carbonate, a such as dimethyl carbonate (DMC), methylethyl carbonate (MEC), methylpropyl carbonate (MPC), butylmethyl carbonate (BMC), and diethyl carbonate (DEC) and a branched carbonate such as methylisopropyl carbonate (MIPC), isobutylmethyl carbonate (IBMC), sec-butylmethyl carbonate (SBMC), and tert-butylmethyl carbonate (TBMC), etc. may be exemplified. These linear carbonates may be used alone or may be used in the combination of two or more thereof.

The cyclic carbonate and cyclic ester or further the linear carbonate are used suitably selected and combined. Note that as the non-aqueous solvent, the cyclic carbonate is used in an amount of 5 to 50% by volume, the cyclic ester 5 to 75% by volume, and the linear carbonate 0 to 70% by volume.

In the present invention, by using, in particular, a butylmethyl carbonate having a branched C_4H_9 group as the linear carbonate, it is possible to improve the wettability with respect to the separator and possible to efficiently inject the electrolyte in the production of a lithium battery.

As the butylmethyl carbonate having a branched C_4H_9 group, isobutylmethyl carbonate, sec-butylmethyl carbonate, and tert-butylmethyl carbonate may be mentioned. The content is preferably 10 to 70% by volume, based upon the non-aqueous electrolyte composed of the cyclic carbonate and cyclic ester or further optionally the linear carbonate.

[0013]

As the electrolyte salt used in the present invention, for example, $LiBF_4$ may be mentioned. This is used dissolved in the non-aqueous solvent at a concentration of usually 0.1 to 3M, preferably 0.5 to 1.5M.

[0014]

The non-aqueous electrolyte of the present invention is obtained by, for example, mixing the cyclic carbonate and cyclic ester and optionally further the linear carbonate, dissolving the salt therein and dissolving the vinyl sulfone derivative having the formula (I).

[0015]

As the cathode active material, a complex metal oxide of at least one metal selected from the group consisting of cobalt, manganese, nickel, chrome, iron, and vanadium with lithium is used. As such a complex metal oxide, for example, $LiCoO_2$, $LiMn_2O_4$, $LiNiO_2$, etc. may be mentioned.

[0016]

The cathode is prepared by, for example, mixing the cathode active material with a conductive agent such as acetylene black or carbon black and a binder such as polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) and a solvent to make a cathode paste, then coating the cathode paste on a collector such as aluminum foil or a stainless steel foil or lath, drying, compression molding, then heat treating at a temperature of at 50 to 250°C for about 2 hours in vacuum.

[0017]

As the anode active material, lithium metal or a lithium alloy and a carbonaceous material having a graphite-type crystal structure capable of intercalate and disintercalate lithium (heat cracked carbons, coke, graphite (artificial graphite, natural graphite, etc.), an organic polymer compound sintered product, carbon fiber), a complex tin oxide, etc. may be used. In particular, a carbonaceous material having a graphite-type crystal structure having a lattice spacing (d_{002}) of the lattice face (002) of 0.335 to 0.340 nm is preferably used. Note that the powder material such as the carbonaceous material is mixed with a binder such as ethylenepropylene diene terpolymer (EPDM), polytetrafluoroethylene (PTFE), or polyvinylidene fluoride (PVDF) to make an anode paste.

[0018]

The structure of the lithium secondary battery is not particularly limited. A coin battery having a cathode, anode, single layer or multiple layer separator and further a cylindrical battery, prismatic battery, etc. having a cathode, anode, and roll-shaped separator may be mentioned as examples. Note that as the separator, a known polyolefin porous film, woven fabric, nonwoven fabric, etc. is used.

[0019]

[Examples]

Next, the present invention will now be specifically explained by the Examples and Comparative Examples.

Example 1

[Preparation of Non-Aqueous Electrolyte]

A non-aqueous solvent of EC:GBL (volume ratio) = 1:2 was prepared, and $LiBF_4$ was dissolved therein to a concentration of 1M to prepare the non-aqueous electrolyte. Thereafter, divinyl sulfone (R=vinyl group) was added to 1.0% by weight, based upon the non-aqueous electrolyte as the vinyl sulfone derivative (i.e., additive).

[0020]

[Manufacture of Lithium Secondary Battery and Determination of Battery Characteristics]

80% by weight of $LiMn_2O_4$ (a cathode active material), 10% by weight of acetylene black (a conductive agent) and 10% by weight of polyvinylidene fluoride (a binder) were mixed. Then, 1-methyl-2-pyrrolidone was added and mixed therewith. The resultant mixture was coated on an aluminum foil, dried, compression molded, and heat treated to form the cathode. 90% by weight of artificial graphite (an anode active material) and 10% by weight of polyvinylidene fluoride (binder) were mixed. 1-methyl-2-pyrrolidone was added and mixed therewith. The resultant mixture was coated on a copper foil, dried, compression molded, and heat treated to form the anode. A separator of a polypropylene porous film was used and the above electrolyte was injected to prepare a coin battery (i.e., diameter 20 mm, thickness 3.2 mm).

The above coin type battery was charged at room temperature (20°C) by a 0.8 mA constant current and constant voltage for 5 hours to an end voltage of 4.2V, then was discharged under a constant current of 0.8 mA to an end voltage of 2.7V. This charging and discharging was repeated. The initial charging and discharging capacity was about the same as with the case of use of 1M $LiPF_6$ EC:GBL (volume ratio) = 1:2 as an electrolyte (Comparative Example 1). The battery characteristics after 50 cycles were determined, whereupon the retaining rate of the discharging capacity, when the initial discharge capacity was 100%, was 91.3%. Further, the low temperature characteristics were also good. The manufacturing conditions of coin batteries and the battery characteristics of the same are shown in Table 1.

[0021]

Example 2

The same procedure was followed as in Example 1 except for using as the additive divinyl sulfone (R=vinyl group) in an amount of 0.3% by weight, based upon the electrolyte to prepare the non-aqueous electrolyte and prepare a coin battery. The battery characteristics were determined after 50 cycles, whereupon the discharge capacity retaining rate was 90.2%. The manufacturing conditions of the coin battery and the battery characteristics are shown in Table 1.

[0022]

Example 3

The same procedure was followed as in Example 1 except for using as the additive divinyl sulfone (R=vinyl group) in an amount of 5.0% by weight, based upon the electrolyte to prepare the non-aqueous electrolyte and prepare a coin battery. The battery characteristics were determined after 50 cycles, whereupon the discharge capacity retaining rate was 90.7%. The manufacturing conditions of the coin battery and the battery characteristics are shown in Table 1.

[0023]

Example 4

The same procedure was followed as in Example 1 except for preparing a non-aqueous solvent of EC-PC-GBL (volume ratio = 35:5:60), dissolving $LiBF_4$ therein to a concentration of 1M to prepare a non-aqueous solvent, then using as an additive divinyl sulfone (R=vinyl group) in an amount of 2.0% by weight, based upon the non-aqueous electrolyte to prepare the non-aqueous electrolyte and prepare a coin battery. The battery characteristics were determined after 50 cycles, whereupon the discharge capacity retaining rate was 90.4%. The manufacturing conditions of the coin battery and the battery characteristics are shown in Table 1.

[0024]

Example 5

The same procedure was followed as in Example 1 except for preparing a non-aqueous solvent of EC-GBL-IBMC (volume ratio) = 30:50:20, and $LiBF_4$ was dissolved therein to a concentration of 1M to prepare a non-aqueous solvent, then using as an additive divinyl sulfone (R=vinyl group) in an amount of 2.0% by weight, based upon the non-aqueous electrolyte to prepare the non-aqueous electrolyte and prepare a coin battery. The battery characteristics were determined after 50 cycles, whereupon the discharge capacity retaining rate was 91.8%. The manufacturing conditions of the coin battery and the battery characteristics are shown in Table 1.

The wettability of the separator by this electrolyte was determined, whereupon the contact angle was 50.4 degrees.

In the present invention, the wettability of the separator by the electrolyte was determined by the following apparatus. The measurement conditions were an atmosphere of a temperature of 23°C and a humidity of 50%. The contact angle immediately after formation of liquid drops was determined for a separator upon which the non-aqueous electrolyte was dropped. The measurement apparatus was an image processing type contact angle meter Model CA-X made by Kyowa Kaimen Kagaku K.K. The smaller the determined contact angle, the better the wettability of permeability of the separator by the

non-aqueous electrolyte.

[0025]

Example 6

The same procedure was followed as in Example 1 except for using natural graphite instead of artificial graphite as the anode active substance and preparing a non-aqueous solvent of EC-GBL-IBMC (volume ratio) = 30:50:20, dissolving $LiBF_4$ therein to a concentration of 1M to prepare a non-aqueous solvent, then using as an additive divinyl sulfone (R=vinyl group) in an amount of 2.0% by weight, based upon the non-aqueous electrolyte to prepare the non-aqueous electrolyte and prepare a coin battery. The battery characteristics were determined after 50 cycles, whereupon the discharge capacity retaining rate was 91.5%. The manufacturing conditions of the coin battery and the battery characteristics are shown in Table 1.

The wettability of the separator by this electrolyte was determined, whereupon the contact angle was 50.4 degrees.

[0026]

Comparative Example 1

A non-aqueous solvent of EC:GBL (volume ratio) = 1:2 was prepared, and $LiBF_4$ was dissolved therein to a concentration of 1M. At this time, no vinyl sulfone derivative was added. This non-aqueous electrolyte was used to prepare a coin battery in the same way as in Example 1 and determine the battery characteristics. The discharge capacity retaining rate after 50 cycles was 75.6% of the initial discharge capacity. The manufacturing conditions of the coin battery and the battery characteristics are shown in Table 1. The wettability of the separator by this non-aqueous electrolyte was determined, whereupon the contact angle was 77.2 degrees, the wettability was poor.

[0027]

[Table 1]

Table 1

	Cathode	Anode	Additive	Amount added (wt%)	Electrolyte composition (volume ratio)	50 cycle discharge capacity retaining rate (%)
Ex. 1	$LiMn_2O_4$	Artificial graphite	Divinyl sulfone	1.0	IM $LiBF_4$ EC/GBL=1/2	91.3
Ex. 2	$LiMn_2O_4$	Artificial graphite	Divinyl sulfone	0.3	IM $LiBF_4$ EC/GBL=1/2	90.2
Ex. 3	$LiMn_2O_4$	Artificial graphite	Divinyl sulfone	5.0	IM $LiBF_4$ EC/GBL=1/2	90.7
Ex. 4	$LiMn_2O_4$	Artificial graphite	Divinyl sulfone	2.0	IM $LiBF_4$ EC/PC/GBL = 35/5/60	90.4
Ex. 5	$LiMn_2O_4$	Artificial graphite	Divinyl sulfone	2.0	IM $LiBF_4$ EC/GBL/IBMC = 30/50/20	91.8
Ex. 6	$LiMn_2O_4$	Natural graphite	Divinyl sulfone	2.0	IM $LiBF_4$ EC/GBL/IBMC = 30/50/20	91.5
Comp. Ex. 1	$LiMn_2O_4$	Artificial graphite	None	0.0	IM $LiBF_4$ EC/GBL=1/2	65.6

[0028]

Note that the present invention is not limited to the described examples. Various combinations easily deducible from the gist of the invention are also possible. In particular, the combinations of solvents in the examples are not limitative. Further, the above examples related to coin batteries, but the present invention may also be applied to cylindrical batteries and prismatic battery.

[0029]

[Effect of the Invention]

According to the present invention, it is possible to provide a lithium secondary battery having superior battery cycle characteristic and battery characteristics such as electrical capacity, storage characteristic.